

*FINAL*  
**PROGRESS REPORT**

**MECHANISMS OF PHOTOREFRACTIVITY IN POLYMERIC MATERIALS**

Principal Investigator: Prof. W. E. Moerner

Co-Investigator: Prof. Jay Siegel

Department of Chemistry and Biochemistry, University of California, San Diego  
Mail Code 0340, 9500 Gilman Drive  
La Jolla, California 92093-0340  
619-822-0453 (office), 619-534-7244 (fax), e-mail: wmoerner@ucsd.edu

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## 2. Objectives:

The objectives of this program have been multifaceted and interdisciplinary: to develop new photorefractive polymers with high gain, diffraction efficiency, and speed; to demonstrate previously unobserved physical effects such as optical limiting, beam fanning, and self-pumped phase conjugation which may be important for Air Force application; and most importantly, to perform detailed physical measurements and analysis to understand the mechanisms controlling the optical performance and processing behavior of photorefractive polymers.

## 3. Status of Effort: (200 words)

This grant has featured a multi-pronged effort to develop new photorefractive polymers, demonstrate previously unobserved physical effects, and most importantly, to understand the mechanisms controlling the performance. Significant progress has occurred in all areas. In the synthetic area, a modular approach to the synthesis of fully-functional photorefractive polymers has been developed based on grafting of various functional components onto siloxane polymers and post-graft chemical modifications, and novel charge transporting agents and sensitizers have been prepared. We have thoroughly explored the class of host-guest photorefractive polymers based on poly(n-vinyl carbazole) and dicyanostyrene-containing nonlinear optical chromophores. These materials have shown gain coefficients up to  $200 \text{ cm}^{-1}$ , single-pass gain factors of 500 times, and grating growth times as small as 4 ms at  $1 \text{ W/cm}^2$ . These extremely high performance levels have led to the first observations in any photorefractive polymer of beam fanning, self-pumped phase conjugation, and the detection of laser-based ultrasound under this grant. In the mechanistic area, for the first time the active trapping species has been identified to be the fullerene anion, and the compensator species as the nonlinear optical chromophore. This new insight should allow future optimization of space-charge field, the phase shift, resolution, the maximum index modulation, and even the trap-related influences on the speed.

## 4. Accomplishments/New Findings:

(publications are numbered according to the list in the Attachment)

### A. Preparation of photorefractive polymer composite samples

Although a high performance photorefractive material exhibiting a gain coefficient of  $200 \text{ cm}^{-1}$  was discovered by the Arizona group in 1994, attempts by other groups to reproduce the results proved elusive. The main reason for this was the rapid crystallization which can occur for highly doped composite photorefractive polymers. Our efforts to improve the material stability have involved selecting a compatible plasticizer (butyl-benzyl-phthalate, BBP) which is not prone to crystallization itself, as is ethylcarbazole (ECZ). Furthermore, ensuring the purity of the constituents by repeated recrystallization (for instance, PVK was purified twice by dripping into boiling ethanol) seemed to improve slightly on the stability problems, but more importantly it led to more reproducible photorefractive properties. The major advance, however, was in sample processing. After dripping, the samples were dried in the oven for 15 hrs at  $90^\circ\text{C}$  before sandwiching. Samples prepared in this way have shown greatly reduced crystallization (the oldest sample is now some 36 months old). Moreover, we are

now able to apply much higher electric fields before breakdown. We believe that these improvements are due to (1) a better extraction of residual solvent, and (2) to better mixing of the components, as this temperature is very close to the melting point of the chromophores as determined from the modulated differential scanning calorimeter. The model material receiving the most study to date to be described below has the composition PVK:35%PDCST:15%BBP:0.5%C<sub>60</sub> where PDCST stands for the piperidinodicyanostyrene chromophore. [Publication 140]

### **B. Observation of simplified photoconductive behavior**

From standard photoconductivity measurements at varying intensities, we observed that the maximum photoconductivity varied with intensity as  $I^{0.86}$ . This nearly linear dependence suggests that a simple one-level band-transport model may adequately account for the photoconductivity in this polymer composite, in contrast to the complex sublinear behavior arising from shallow traps observed for other polymeric composites. In addition, the photoconductivity exceeds the dark conductivity of the sample at a very low intensity, estimated to be 0.7 mW/cm<sup>2</sup>. For several previously studied materials, far higher intensities were required to make the photoconductivity dominant. This behavior may be useful in increasing the operating speed of PR polymers, as required for some AF applications in optical processing and limiting. In addition, the photoconductivity increases rapidly with increasing applied field. This rapid rise may be attributed to the electric field dependence of the carrier-generation quantum efficiency and the carrier mobility. The quantum yield was estimated by assuming that all photo-excited carriers are collected at the electrodes (i.e. that carrier transit time,  $\tau_{\text{transit}}$  is smaller than the recombination time,  $\tau_r$ ); the quantum yield follows a power law with increasing field due to geminate recombination effects. [Publication 135]

### **C. Measurement of two-beam coupling gain**

Two-wave mixing was performed by interfering two writing beams (both P-polarized) inside the polymer sample while monitoring the output intensities with a powerful new LabView program. In a typical experimental run we obtain the gain, the modulation amplitude of the refractive index, and the grating phase with respect to the interference pattern, all at once. As expected, we see a large increase of the coupling coefficient with increasing applied electric field which has come to be expected from this class of low-T<sub>g</sub> photorefractive polymers in which both the space-charge field and the electro-optic response, being well below their saturation values, increase linearly with applied field. At the highest fields, two-beam coupling gain coefficients as large as 200 cm<sup>-1</sup> have been observed in our material PVK:PDCST:BBP:C<sub>60</sub>, far above the optical loss coefficient of 12 cm<sup>-1</sup>. This high two-beam coupling gain coefficient is accompanied by fast response time ( $\tau_g=50$  ms at 1W/cm<sup>2</sup> 676nm light), over-modulation of diffraction efficiency, and high sensitivity ( $S_{nl}\cong 3$  cm<sup>3</sup>/kJ). Furthermore, it is evident that high fields also increase the speed of grating build-up, which is not surprising considering that the rise-time is directly proportional to the dielectric relaxation time and consequently depends inversely on the product of the field dependent quantum efficiency and carrier mobility. More thorough study of the large gains will continue, and we expect that new nonlinear effects will be observed which may be useful for applications. [Publication 140]

#### **D. Observation of overmodulation of diffraction efficiency**

We have completed measurements of the diffraction efficiency as a function of the electric field using a second new LabView program written by Dr. Grunnet-Jepsen. The diffraction efficiency clearly shows overmodulation as predicted by Kogelnik for diffraction from a static volume hologram with large index modulation (at the first maximum,  $\Delta n = 3 \times 10^{-3}$ ). The diffraction efficiency reaches a maximum of 45%, short of the theoretically attainable 100% partially due to optical absorption in the sample. It is however interesting to note that the experimental results show a remarkably good fit to diffraction from a uniform volume grating with a coupling coefficient which varies as  $E^2$ . This suggests that the saturation space charge field,  $E_q$ , at our grating spacing must be greater than the projection of the electric field on the grating vector, or  $E_q > 260$  kV/cm. [Publication 135]

#### **E. Fully-Functional, Low- $T_g$ Photorefractive Polymers**

Given the need for non-linear optical (NLO) and charge transport (CT) components in an amorphous photorefractive film, we designed and synthesized a siloxane-based low  $T_g$  material with both components on one polymer backbone. We discovered that hydrosilation chemistry, normally used to adorn polysiloxanes with homogeneous substituents, tolerates mixtures of hydrosilation precursors and thus permits the formation of stochastically scrambled A, B substituted polymers. In addition, we found that the siloxane backbone would tolerate common reaction conditions used for the condensation or coupling of NLO or CT fragments. Although the hydrosilation efficiency was not equal over all substrates, we found that the substitution rates for different precursors were close enough to allow us to control the composition of polymer substitution by simple variation of the ratios of the precursors. These useful synthesis findings have made it possible a) to synthesize fully functional polymers routinely; and b) to vary polymer composition to effect detailed structure-activity studies directed at our goal of understanding mechanistic aspects of these materials. Evidence of success in this area is seen from the close to 20 new multi-functional polymers prepared recently based on carbazole and cyanostyrene derivatives. Additional versatility in the method comes from the ability to start from a commercial source of polysiloxane with precharacterized molecular weight distributions. [Publication 156]

#### **F. Spatial phase-shift determination**

The strength of the photorefractive effect depends critically on the size of the space-charge field, and hence on the density of charge traps available. In order to determine the photorefractive trap density, we used the commonly employed grating translation technique to measure the grating spatial phase shift,  $\phi_p$ , from which the trap density could be deduced. However, it was quickly realized that the gain is so high in the new materials that we had developed, the strong energy- and phase-coupling that takes place during recording will lead to non-uniform slanted (or bent) refractive index gratings. This significantly complicates the analysis of the grating translation data, leading to an apparent dependence of the phase shift on beam ratio and optical polarization. We presented in Pub. [143] analytical solutions of the effect of grating translation for the special case of  $\phi_p = \pi/2$ . For the general case of  $\phi_p \neq \pi/2$ , numerical solutions were compared with measurements in a photorefractive polymer. One of the important conclusions of this work is that to correctly determine the phase-shift it becomes necessary to (1) carry out a complex numerical modeling of the measured data, or (2) to perform the measurements for weak beam coupling (e.g. s-polarized beams) and a beam ratio of 1. The latter approach is usually to be preferred.

### **G. High trap density achieved**

Having developed a new method for the determination of the photorefractive phase-shift, we investigated PVK:PDCST:BBP:C<sub>60</sub> in detail using optical two-wave mixing gain measurements in conjunction with the grating translation technique for determination of the photorefractive phase-shift. An effective trap density of  $N_{\text{eff}}=1.5 \times 10^{17} \text{ cm}^{-3}$  was estimated from the dependence of the phase-shift on the grating spacing (grating wavevector) and the applied electric field. This value of the trap density is approximately 3-10 times larger than previously achieved in *any other material*, including the inorganic crystals. Large trap densities allow good performance at high resolution (i.e., small grating spacings), which makes this material very well-suited for hologram recording in the reflection geometry. Furthermore, the theory of orientational enhancement was successfully utilized to explain the field-dependence of the observed photorefractive response, and in this low-glass-transition temperature system the modulation of the refractive index was shown to stem primarily from the spatial modulation of the birefringence [Publication 145].

### **H. Large single-pass gain factor of 5 observed in multilayer samples**

Since many applications are concerned with the overall gain factor (i.e. signal amplification) rather than with the gain coefficient, it is important to demonstrate large gains if these new materials are to have any impact on applications. We found that the gain could be increased by simply sandwiching several samples together to form multi-layered structures [Pub. 144]. Thus, we demonstrated that the apparent limitations imposed by electrical break-down and the high voltage power supply could be overcome by adopting a multi-layer approach. In this way, we showed that the gain could be increased from a factor of 1.6 for a single layer structure (with an applied field of 60V/ $\mu\text{m}$ ), to 2.5 with a 2 layer structure, and to 5 with a three layer structure.

### **I. Extremely large single-pass gain factor of 500 observed with moving gratings**

We have shown that the use of moving gratings allows dramatic enhancement of the two-beam coupling gain in these photorefractive polymers. This technique, which is well-known to enhance the gain coefficients in inorganic crystals with a high mobility-lifetime product, involves the slight detuning of one of the two-wave mixing beams before the two beams interfere inside the material. This detuning of a few Hz results in an interference pattern which sweeps ("runs") slowly across the material. The beneficial effects of detuning were clearly evident experimentally for our new polymers. For no detuning, the degenerate two-beam coupling gain was  $\sim 2.5$  giving  $\Gamma=62 \text{ cm}^{-1}$  for a sample of thickness 140  $\mu\text{m}$  and a field of 71 V/ $\mu\text{m}$ . As the detuning frequency is increased the gain increases rapidly, reaches a maximum value of 14 ( $\Gamma=179 \text{ cm}^{-1}$ ) at the optimum detuning frequency. Moreover, when this method was used in conjunction with the multi-layer approach, a small signal optical amplification as large as a factor of 500 was achieved using a three-layer sample! This is the highest gain reported to date in any photorefractive polymer. From an investigation of the time dependence and detuning frequency dependence, we were able to determine that hole conduction is dominant and that the mobility life-time product reaches  $\mu\tau=3 \times 10^{10} \text{ cm}^2/\text{V}$  at an applied electric field  $E_0=71 \text{ V}/\mu\text{m}$ . [Publication 146]

### **J. Beam Fanning and Optical Limiting**

In the process of examining our photorefractive polymer system in detail, we discovered that

beam fanning is prominent for large electric fields, seriously compromising normal two-beam coupling gain. This was the first observation of beam fanning (amplified scattering of light) in a photorefractive polymer [Publication 137]. Beam fanning in PR polymers is manifested by the amplification of light scattered in the plane of the sample, since it is these beam which experience the greatest  $\Gamma L$  (gain coefficient – interaction length product). This means that beam fanning in polymers can be controlled by changing the polarity of the applied electric field so that the gain is in the direction away from the plane of the sample. We note further that since the transmitted pump beam is significantly depleted by fanning (ca. 40%), this process may be used in optical limiting/filtering applications if several PR samples are sandwiched together to augment the fanning losses [Publication 147].

#### **K. Self-Pumped Phase-Conjugation and Oscillation**

Having fabricated a material with a large gain coefficient, and having shown that the real gain can be significantly increased by using multi-layered structures as well as moving gratings, it became evident that a system could be designed that would have enough signal amplification to permit the setting up of a linear resonator. Using a 2-layer sample placed in an optical cavity made with two concave mirrors, with only one laser beam incident, spontaneous oscillation due to two-beam coupling gain has been observed. Because only one pumping beam is required, this configuration also acts as a self-pumped phase conjugating mirror with a reflectivity of 13% for an applied electric field of 75 V/ $\mu\text{m}$ . When the cavity oscillation starts, the transmitted pump beam is attenuated by almost a factor of 10, suggesting possible applications in optical limiting. Previously, this effect has only been observed in a few special inorganic crystals like BaTiO<sub>3</sub> and SBN, thus marking a crucial milestone for the growing new class of photorefractive polymers. [Publication 144]

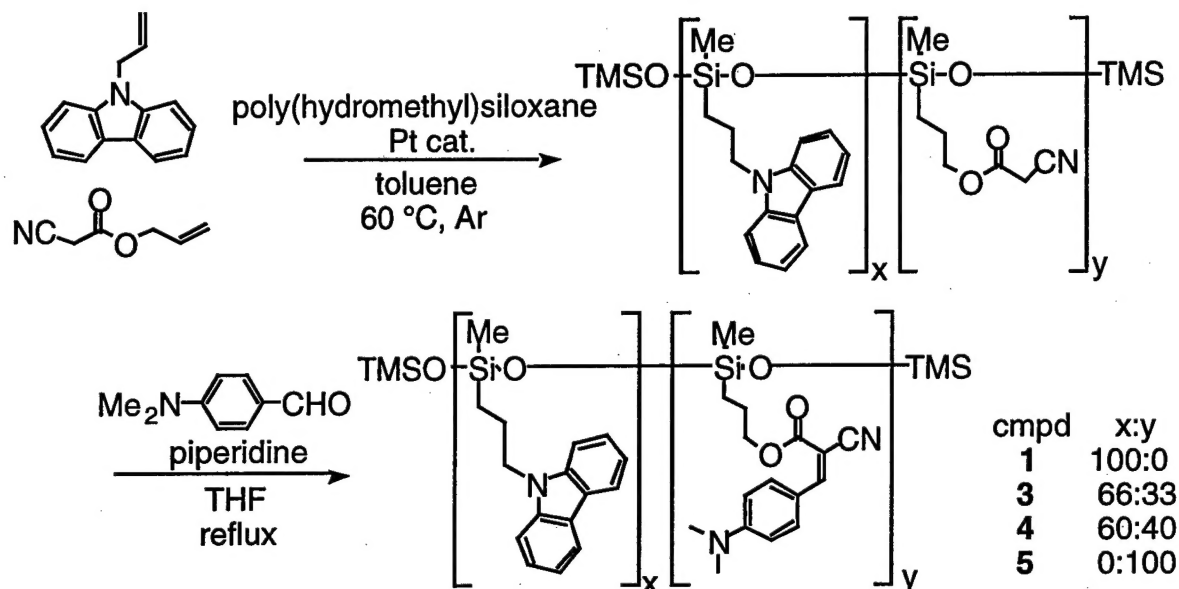
#### **L. Poly-Functional, Low-T<sub>g</sub> Photorefractive Polymers**

Expanding on our discovery that hydrosilation chemistry in combination with condensation methods could produce polyfunctional photorefractive (PR) materials, we prepared new bifunctional polymeric materials with covalently attached non-linear optical (NLO) and charge transport (CT) components. An example of this is shown in Scheme 1 (next page) in which a carbazole transporting agent and a NLO chromophore have been attached to a poly(siloxane) backbone. The poly(siloxane) backbone was chosen due to its inherently low glass transition temperature, reflecting the desire to profit from the orientational enhancement effect. These new materials were fully evaluated in the PR characterization system and polymer 4 for example showed net gain, with a gain coefficient of 22 cm<sup>-1</sup> with a background absorption at 676 nm of 5.4 cm<sup>-1</sup>. The full report of the synthesis and PR properties of these materials is described in Publication 156.

In the course of this synthetic research, we developed ways to control the orientation of the connection of the NLO component to the backbone as well as its mobility. We were also able to attach new CT agents other than carbazole, such as aryl amines. In addition, we found that the charge generator species could also be attached to the backbone via a modified C<sub>60</sub> molecule. This technology was the remaining link to our goal of producing libraries of truly fully-functionalized PR materials. The effectiveness of this modified CG in PR applications is being evaluated. The library method allowed us to tune the PR properties of a polymer by alterations in the ratios of the components in a range where the non-covalent composite showed serious stability and sample preparation problems. Consistently, materials

from new molecular structures yield more easily to sample preparation than their non-covalent counterparts. The hydrosilation efficiency is not equal over all substrates, and we found that as more variety is placed into the structure pool more information is needed to control substitution rates and the ratios of the components on the polymer. Preliminary work on conducting backbones has opened up new synthetic challenges.

**Scheme 1**



### M. First Identification of the Trapping Sites and Compensator Species in a PR Polymer

We have discovered several new and important aspects of the trapping states and dynamics in fullerene-doped PR polymers, and this information should be useful in understanding trapping in other PR polymers as well. We often utilize  $C_{60}$  as a sensitizer for our high-performance composite samples, which have shown high gain coefficient ( $\sim 200 \text{ cm}^{-1}$ ), high gain factor (500x single-pass), and even high speed (4 ms at  $1 \text{ W/cm}^2$  – see the next section). We realized that the  $C_{60}$  anion is crucial to the trapping dynamics, and showed that *optical measurement of the sample absorption at 1.08 microns wavelength can be used to follow the  $C_{60}$  anion concentration in as-made PR polymer samples.* This concentration measurement was compared with a holographic determination of the PR trap density by fitting the dependence of the gain coefficient on applied electric field as usual. The two measurements agreed closely, *proving that the  $C_{60}$  anion provides the principal trapping center for photorefractivity in these materials.* By additional spectroscopic measurements as a function of time and irradiation at 647 nm, we showed that the nonlinear optical chromophore acts as a compensator, allowing a background concentration of  $C_{60}$  anion to build up with time. [Publication 153]

The significance of these results is three-fold. First, the principal trapping sites have been identified for the first time in any PR polymer. Second, the compensating centers have been identified, and they are likely to play a role in the time response of the samples. Third, these useful facts provide a framework for the rational design of new PR polymers, as the NLO chromophore is now no longer a passive component, but its energy levels must be taken into account in controlling the all-important photorefractive trap density in the final materials. Control of the trap density leads to control of the space-charge field, the phase shift, and the index modulation, and we are now in a position to influence these properties as required for specific applications. All this has been accomplished with a simple near-infrared spectroscopic measurement on the as-made materials, coupled with our detailed analysis of the PR characteristics.

#### **N. Observation of Fast Photorefractive Response Times Allowing Video Frame Rates**

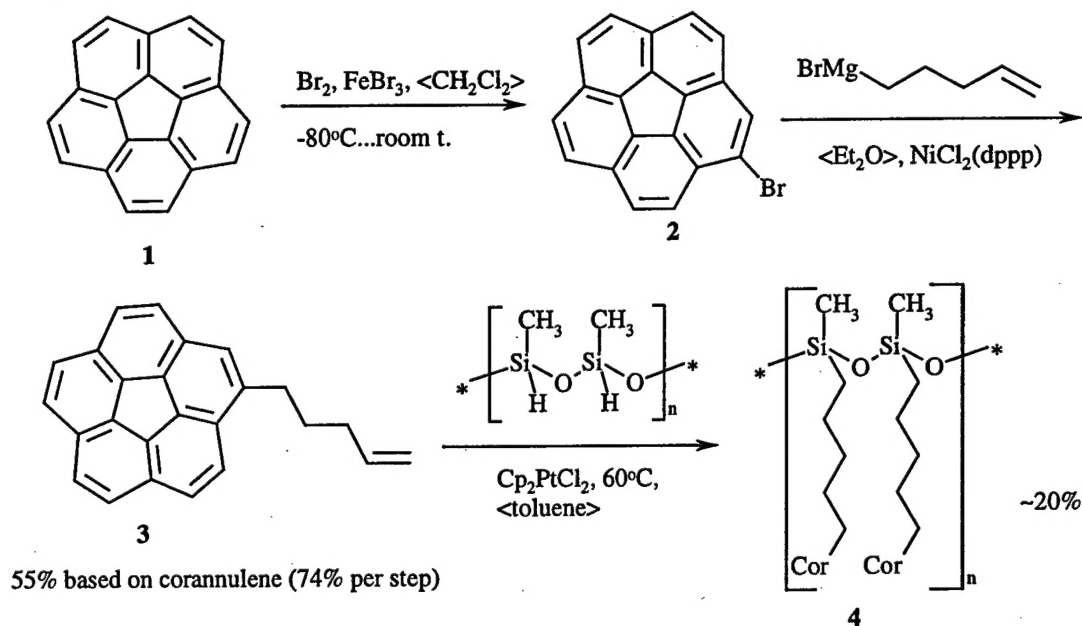
Two novel photorefractive polymer composites have been identified that exhibit the fastest response times reported to date ( $\tau_g \approx 5$  ms at  $1 \text{ W/cm}^2$ ), while maintaining large gain coefficients ( $\Gamma \approx 230$  and  $130 \text{ cm}^{-1}$ ). These materials show promise for video-rate optical processing applications. The materials are based on the composition PVK:NLO:BBP:C<sub>60</sub>, a class of materials which we have been investigating for some time. The NLO chromophores showing the fastest response were AODCST and 7-DCST. [Publication 158]

In order to understand the specific factors controlling the speed in these materials, we have measured both the photoconductivity and the speed (inverse response time) as a function of intensity and applied electric field. In both cases, the shapes of the curves are very similar, indicating that the speed is mostly determined by the photoconductivity, not by the orientational response time of the NLO chromophores in these low T<sub>g</sub> composites. We believe that these materials are fast because we have utilized NLO chromophores which have relatively shallow trapping energetics (AODCST and PDCST), so that the hindrance to the charge motion is minimized. We have obtained additional examples of this trend by correlating the normalized speed of response with the depth of the NLO compensator for every NLO in a series of DCST derivatives and find very good correlation – slower materials have deeper compensating traps. [Publication 163]

To validate this model, further proof is required from time-of-flight measurements of charge carrier mobility, which is a topic of proposed future research in the near future and during the renewal period.

#### **O. New Photoconductor**

Corannulene (1) is a bowl-shaped twenty-carbon-fragment with interesting electronic properties. Nothing was known about its possible photoconducting properties. Its oxidation potential of (-2.25V vs Ag/AgNO<sub>3</sub> in CH<sub>3</sub>CN) implies that it would be a possible electron conductor, which could lead to a new parameter space for photorefractive polymers. To investigate this, a polysiloxane-based corannulene was synthesized, as outlined in Scheme 2.

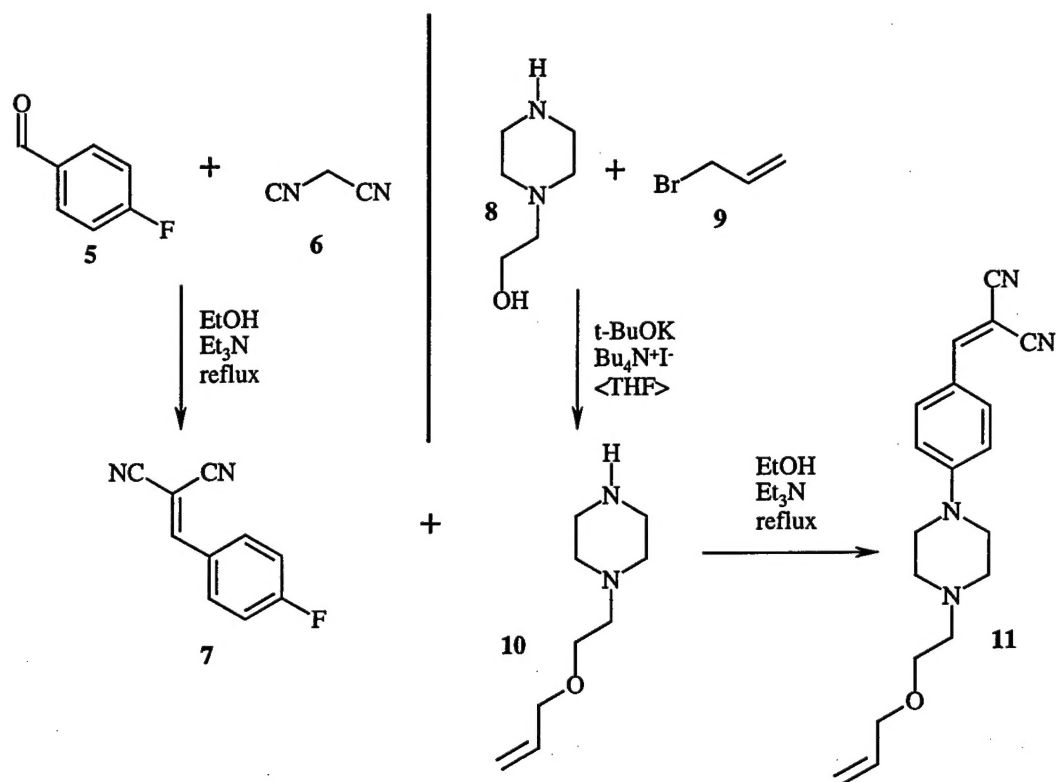


Scheme 2

Corannulene was synthesized by a 11-step route and brominated to yield **2** (Borchardt, A.; Fuchicello, A.; Kilway, K.V.; Baldrige, K.K.; Siegel, J.S. *J. Am. Chem. Soc.* **1992**, *114*, 1921-1923). It is then coupled with 5-bromo-1-pentene (nickel-catalyzed Kumada-coupling with the Grignard-compound) to give the Pentenylcorannulene **3**. The synthesis of the polymer **4** is performed as usual. The photophysical properties of this new polymer are still under investigation using a recently-obtained mobility measurement apparatus.

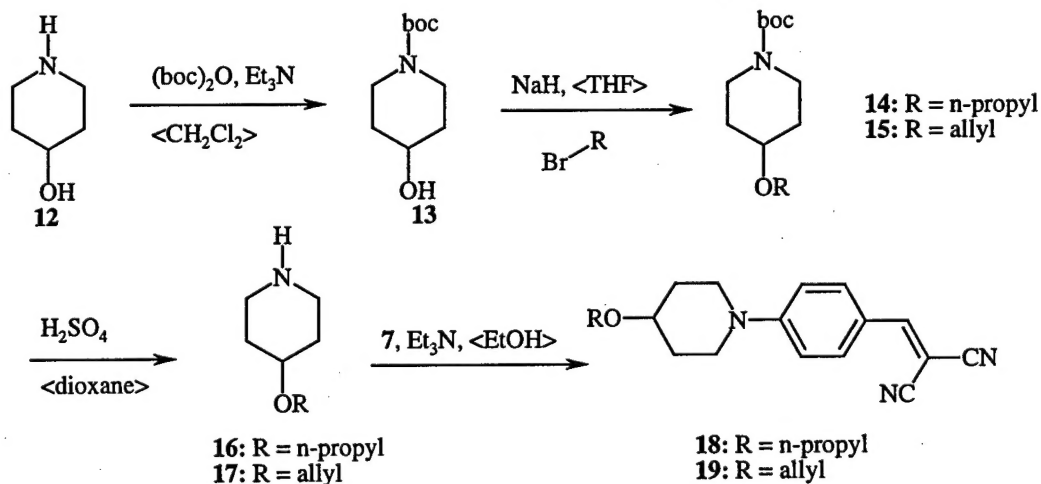
## P. New Chromophores and mixed Polymers

PR-samples containing the NLO-chromophore 4-piperidinobenzlidenemalonitrile (PDCST), poly(N-vinyl carbazole) (PVK) as charge transporting agent and C<sub>60</sub> as sensitizer have shown an excellent performance (Grunnet-Jepsen, A.; Thompson, C.L.; Moerner, W.E. *J. Opt. Soc. Am. B* **1998**, *15*, 905-913). This class of NLO-chromophores with a terminal olefin could be incorporated into polysiloxane leading to a monofunctional polymer with enhanced hyperpolarizability. To test these possibilities, the synthesis of **11** (Scheme 3) was completed. Preliminary test with **11** showed decomposition when made into a PR-sample with PVK and C<sub>60</sub>. When **11** was heated independently the absorbance spectra shows high absorbance at the operating wavelength of the lasers. However, its absorbance at 650 nm is quite low before heating, indicating the molecule is not suitable for PR-samples.



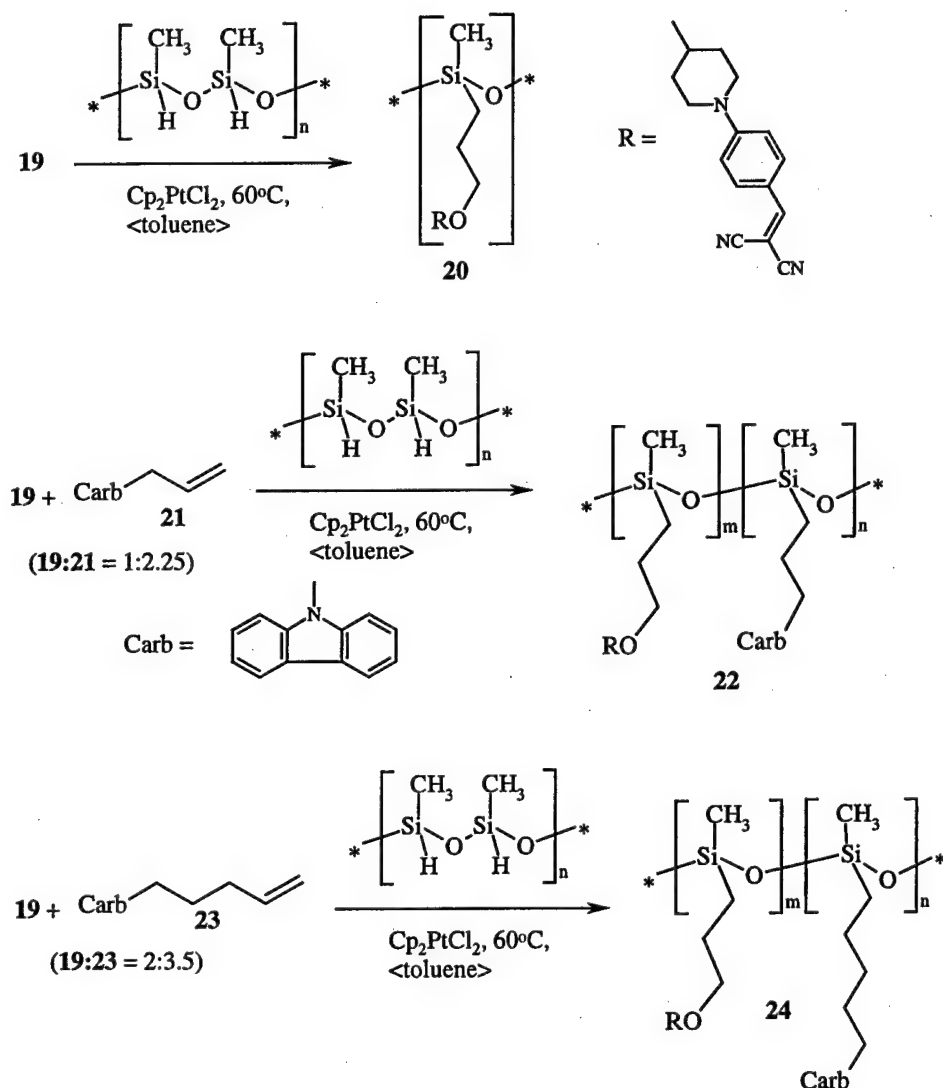
Scheme 3

A likely explanation for the decomposition of **11** when heated is the oxidation of its second electron-rich nitrogen. To avoid the use of piperazine heterocycles a new synthetic route was investigated (Scheme 4) which uses piperidine as the electron donor in the NLO-chromophore. Preliminary PR-samples containing **18**, PVK and C<sub>60</sub> show equivalent performance to PDCST. Since **18** does not decompose when heated this type of NLO-chromophore (**19**) should be a good candidate for polymerization followed by use in PR-samples.



Scheme 4

The polymerization of the new NLO chromophores were carried out in mono-functional form as well as bi-functional (Scheme 5) using carbazole as CTA. Initially it was believed that polymer **20** could be doped with various CTA and CG materials to investigate this type of mono-functional polymer. Unfortunately this polymer was too insoluble in common solvents to make any useful PR samples. However, if the ratios are tuned for bi-functional polymers such as **22** and **24** these materials can be made into high quality PR-samples. Initial results for two-beam-coupling of **24** doped with C<sub>60</sub> show similar performance to PDCST based PR samples.

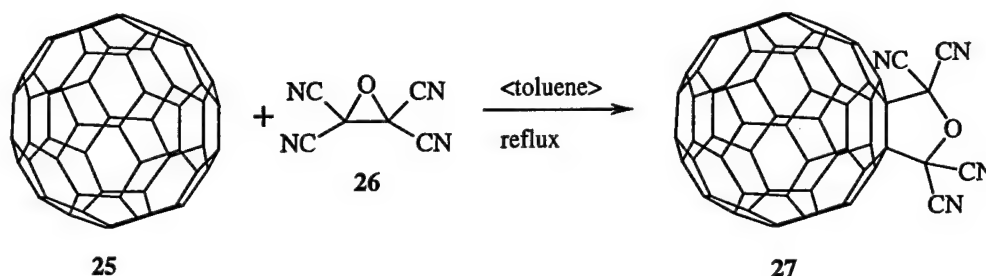


Scheme 5

## Q. New Sensitizer

The need for charge generators which function at longer wavelength in PR samples has inspired the synthesis of **27** (Scheme 6). It was reported that when this derivative of C<sub>60</sub> is

added to PVK measurable photoconductivity for this system was achieved at near-IR wavelengths (Li, F.; Li, Y.; Guo, Z.; Mo, Y.; Fan, L.; Bai, F.; Zhu, D. *Solid State Commun.* **1998**, *107*, 189-192). Not only does this molecule have the potential to work in the IR but also at current wavelengths the photoconductivity is expected to surpass equivalent samples with C<sub>60</sub>, thus providing a path for potential increases in speed.



Scheme 6

## 5. Personnel Supported:

(listed in attachment)

## 6. Publications:

(listed in attachment)

## 7. Interactions/Transitions:

(a) Participations/presentations at meetings, conferences, seminars, etc.

### Invited:

- W. E. Moerner, "Mechanisms of Photorefractivity in Polymer Composites," SPIE Conference on Organic Photorefractive Materials and Xerographic Photoreceptors, Denver, Colorado, August 7-8, 1996.
- W. E. Moerner, A. Grunnet-Jepsen, and C. Thompson, "Mechanisms of Photorefractivity in Polymer Composites," Third International Conference on Organic Nonlinear Optics, Marco Island, Florida, December 16-20, 1996.
- W. E. Moerner, A. Grunnet-Jepsen, and C. L. Thompson, "Observation of Beam Fanning in a Photorefractive Polymer," Materials Research Society 1997 Spring Meeting, San Francisco, California, March 31- April 4, 1997.
- W. E. Moerner, A. Grunnet-Jepsen, and C. L. Thompson, "Recent Advances in Photorefractive Polymer Materials," SPIE Symposium 3147, Nonlinear Optical Properties of Organic Materials X, San Diego, California, July 30 – August 1, 1997.

- W. E. Moerner, "Mechanisms and Applications of Photorefractivity in New Polymer Composites," R. B. Woodward Lecture, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, September 18, 1997.
- W. E. Moerner and A. Grunnet-Jepsen, "Recent Advances in High Gain Photorefractive Polymers," IEEE Lasers and Electro-Optics Society Annual Meeting, San Francisco, California, November 10-13, 1997.
- W. E. Moerner, "Understanding Photorefractivity in Polymers: Materials for an Optical Transistor?" Physical Chemistry Colloquium, University of California, Berkeley, Berkeley, California, January 27, 1998.
- W. E. Moerner, "Photorefractive Polymers: Materials for Optical Processing Applications," Weissberger-Williams Lecture, Eastman Kodak Company, Rochester, New York, February 6, 1998.
- W. E. Moerner, A. Grunnet-Jepsen, B. Smith, and D. Wright, "Recent Advances in Photorefractive Polymer Composites," Dallas National Meeting, American Chemical Society, Dallas, Texas, March 29 – April 2, 1998.
- W. E. Moerner, A. Grunnet-Jepsen, D. A. Wright, and B. R. Smith, "Recent Advances in High Gain Photorefractive Polymers," Conference on Lasers and Electro-Optics CLEO '98, San Francisco, California, May 3-8, 1998.
- M. A. Diaz-Garcia, D. Wright, M. DeClue, J. Casperson, B. R. Smith, W. E. Moerner, and R. J. Twieg, "High-Speed Photorefractive Polymer Composites," Postdeadline Paper, Conference on Lasers and Electro-Optics CLEO '98, San Francisco, California, May 3-8, 1998.
- D. Wright, A. Grunnet-Jepsen, M. A. Diaz-Garcia, J. D. Casperson, B. Smith, M. S. Bratcher, M. S. DeClue, J. S. Siegel, W. E. Moerner, and R. J. Twieg, "Trapping Studies on Photorefractive Polymers," *Proc. Soc. Photo-Opt. Instrum. Engr.* **3471**, 60-71 (1998).
- W. E. Moerner, "Mechanisms of Photorefractivity in Polymer Composites," Summer School on Molecular Optoelectronics, Cursos de Verano, San Lorenzo de El Escorial, Madrid, Spain, August 3-7, 1998.
- W. E. Moerner, "Applications of Photorefractive Polymers," Summer School on Molecular Optoelectronics, Cursos de Verano, San Lorenzo de El Escorial, Madrid, Spain, August 3-7, 1998.
- W. E. Moerner, M. A. Diaz-Garcia, A. Grunnet-Jepsen, D. Wright, M. Bratcher, M. DeClue, J. S. Siegel, R. J. Twieg, "Fast and Efficient Photorefractivity in Polymer Composites," American Chemical Society Annual Meeting Symposium on Organic Thin Films for Photonic Applications, Boston, Massachusetts, August 23-27, 1998.
- W. E. Moerner, M. A. Diaz-Garcia, A. Grunnet-Jepsen, and D. Wright, "Mechanisms for High Gain in Photorefractive Polymers," Optical Society of America Annual Meeting, Baltimore, Maryland, October 4-9, 1998.
- W. E. Moerner, D. Wright, M. Diaz-Garcia, A. Goonesekera, J. Casperson, B. Smith, M. S. DeClue, E. Glazer, J. S. Siegel, and R. J. Twieg, "New Insights into Trapping and Compensation in Photorefractive Polymers," Material Research Society Spring Meeting Symposium F, San Francisco, California, April 5-9, 1999.

W. E. Moerner, A. Grunnet-Jepsen, D. Wright, J. Casperson, E. Glazer, M. DeClue, J. S. Siegel, and R. J. Twieg, "Understanding Trapping in Photorefractive Polymer Composites for Optical Processing Applications," Conference on Lasers and Electro-Optics CLEO '99, Baltimore, Maryland, May 23-28, 1999.

**(b) Consultations to other laboratories and agencies**  
(listed in attachment)

**(c) Transitions**  
(listed in attachment)

**8. New Discoveries, Inventions, or Patent Disclosures:**

Invention Disclosure: W. E. Moerner and A. Grunnet-Jepsen, "Ultrasonic Nondestructive Testing Using a Photorefractive Polymer as an Adaptive Beamsplitter", June 10, 1998; patent application filed.

**9. Honors/Awards:**  
(listed in attachment)

2. Final Program Statistics AFOSR Grant No. F49620-96-1-0135

PI Name: W. E. Moerner

Institution: University of California, San Diego

- (1) Number of PI and Co-PI involved in the research project : 2
- (2) Number of Post Docs Supported under AFOSR: 5
- (3) Number of graduate students supported by AFOSR: 2 (AASERT)
- (4) Number of other researchers supported by AFOSR: 3
- (5) Number of publications by PI's in refereed journals: 45
- (6) Number of publications (in refereed journals only) that acknowledge AFOSR support:  
17
- (7) Awards and Honors received by the PI/co-PI (life-time received): 29

Attachment for Grant No. F49620-96-1-0135

PI Name: W. E. Moerner

Institution: University of California, San Diego

(1) PI and Co-PI involved in the research project :

PI: Prof. W. E. Moerner, Department of Chemistry, UCSD  
co-PI: Prof. Jay Siegel, Department of Chemistry, UCSD

(2) Post Docs Supported under AFOSR:

Anders Grunnet-Jepsen  
Maria A. Diaz-Garcia  
Matthew Bratcher  
Arosha Goonesekera  
Gunter Grube

(3) Graduate students supported under this AFOSR grant:

(none)

(Note: Mike DeClue and Daniel Wright were partially supported with AASERT funds.)

(4) Other researchers supported by AFOSR:

Courtney Thompson (part-time undergraduate)  
Barry Smith (part-time undergraduate)  
Julie Casperson (part-time undergraduate)

(6) Publications (in refereed journals only) that acknowledge AFOSR support:

135. W. E. Moerner, A. Grunnet-Jepsen, C. L. Thompson, and R. J. Twieg, "Mechanisms of Photorefractivity in Polymer Composites," *Proc. SPIE* **2850**, 2 (August 1996).
137. A. Grunnet-Jepsen, C. L. Thompson, R. J. Twieg, and W. E. Moerner, "Amplified Scattering in a High Gain Photorefractive Polymer," *J. Opt. Soc. Am. B* **15**, 901 (1998).
139. W. E. Moerner, A. Grunnet-Jepsen, and C. L. Thompson, "Photorefractive Polymers," *Annual Reviews of Materials Science* **27**, 585-623 (1997).
140. A. Grunnet-Jepsen, C. L. Thompson, and W. E. Moerner, "High-Performance Photorefractive Polymer with Improved Stability," *Appl. Phys. Lett.* **70**, 1515 (1997).
143. A. Grunnet-Jepsen, C. L. Thompson, and W. E. Moerner, "Measurement of Spatial Phase-Shift in High Performance Photorefractive Materials," *Opt. Lett.* **22**, 874 (1997).

# REPORT DOCUMENTATION PAGE

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<b>6. AUTHOR(S)</b> Drs. W. E. Moerner/ J. Siegel				
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<b>13. ABSTRACT (Maximum 200 Words)</b> This grant has featured a multi-faceted effort to develop new photorefractive polymers, demonstrate previously unobserved physical effects, and most importantly, to understand the mechanisms controlling the performance. Significant progress has occurred in all areas. In the synthetic area, a modular approach to the synthesis of photorefractive polymers has been developed based on grafting of various functional components onto siloxane polymers and post-graft chemical modifications. We have thoroughly explored the class of host-guest photorefractive polymers based on poly(n-vinyl carbazole) and dicyanostyrene-containing nonlinear optical chromophores. These materials have shown gain coefficients up to 200 cm <sup>-1</sup> , and single-pass gain factors of 500 times, and grating growth times as small as 4 ms at 1 W/cm <sup>2</sup> . These extremely high performance levels have led to the first observations of beam fanning, self-pumped phase conjugation, and the detection of laser-based ultrasound under this grant. In the mechanistic area, for the first time the active trapping species has been identified to be the fullerene anion, and the compensator species as the nonlinear optical chromophore. This should allow future optimization of space charge field, the phase shift, resolution, and the index modulation.				
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